

CEMENT

AND

CEMENT MANUFACTURE

INCORPORATING "PORTLAND CEMENT"

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Cost of Manufacture of Cement.

ALTHOUGH the scientific and technical aspects of cement production are of absorbing interest, their practical importance depends upon their relation to cost of production. Financial economy is, or should be, the ultimate aim of every technical development that is essayed in cement factories or laboratories, either in its direct form of reducing cost of production, or indirectly by producing a better cement which will be of more intrinsic value to the user.

As to the progress that has been made during recent years in the quality of cement and in the technical efficiency of the manufacturing processes there can be no two opinions, but whether equal improvement has been made in lowering the cost of production is not certain. Comparison with pre-war periods is not easy because each of the main items comprising the cost of manufacture, viz., labour, fuel, and repairs parts, has increased in different ratio; the cost per man-hour shows the greatest increase of the three, and fuel the least. Comparison is also made more difficult because of the improvement in quality since pre-war years, as this has mainly been secured by finer grinding which adds appreciably to the cost.

Apart from anything else it is certain that the capital cost of cement factories has increased beyond the proportion of the "cost-of-living" or the "wholesale index" which represent changes that have taken place in other directions. A fully-equipped cement works nowadays costs at least twice as much as a works erected twenty years ago. This is due largely to the cost of labour-saving devices that are a prominent feature of modern works, mechanical packing plant being the outstanding example. Such equipment provides its return in lower operating costs, although to some extent items in the labour department have merely been replaced by items in the fuel and repair departments of the cost sheets. There will no doubt be an increasing tendency to utilise mechanical plant for handling materials, and the old-time standard of production of six tons of cement per week for each man employed will steadily increase to 20 tons or more.

An even more important step to economy is, however, likely to take place in kiln fuel consumption. Rotary kiln designers are now able to guarantee

fuel consumption of 24 per cent. of dry coal of 12,600 B.T.U. per lb., which, although a marked reduction on the average performance of ten years ago, is still far from satisfactory to those who have studied the theory of the rotary kiln and who realise how much heat is lost in the chimney gases and in radiation. The waste-heat boiler is one means of utilising the heat passing up the chimney and can be made very effective, but it runs contrary to the modern tendency of many industries which is to leave power production to the experts and to buy electricity. Hence, even when reinforced by the application of the slurry filtering process, which by reducing the water in slurry to one-half the original amount makes the kiln exit gases higher in temperature, and therefore more valuable for waste-heat production, it is probable that the waste-heat boiler will not be regarded as the solution of the problem of heat economy in rotary kilns. It is quite legitimately claimed that fuel combustion in cement rotary kilns is more efficient than in any other industry, but the efficiency of heat transmission in rotary kilns is on a much lower plane and it is probably in this direction that future progress will be made.

German Cement News.

A selling organisation called Verkaufskontor fur Ringfreie Werke, G.m.b.H. has been recently set up in Berlin with the object of assisting and co-ordinating sales by cement companies outside the existing federation.

Portland Cement Werke Heidelberg-Mannheim-Stuttgart, A.G. is increasing its capital up to £250,000; this increase of capital is to be devoted to reorganisation and extension schemes.

New Czechoslovakian Cement Works.

It has again been mooted to run a municipal cement works at Prague.

It is reported from Prague that, with the co-operation of the Bohemian Union Bank, a new cement works is to be erected at Stampfen, near Presburg. The proposed capital of this company is provisionally fixed at £36,800. The works will have a yearly production of 50,000 to 60,000 tons.

New Cement Works for Jugo-Slavia.

The establishment of a new cement works at Sucurac, near Split, by a Belgian financial group is reported from Belgrade. The new works are stated to surpass in productive capacity all existing Jugo-Slavian cement factories. There are to be four rotary kilns, and the cost of the mechanical installation is estimated at £362,000.

Latvian Tariffs on Cement.

The Latvian Government has increased the tariff on cement, and we understand that the Rigaer Zementfabrik has increased its capacity from 35 to 65 thousand tons per annum.

The Spray Process of Slurry Feed.

By S. J. M. AULD, O.B.E., M.C., D.Sc.

THE cement industry being largely dependent on the efficient use of fuel, it is natural that the study of heat transfer phenomena should be the basis for the design of much of its important equipment. In this matter, as reflected by fuel consumption, the change from the dry process to the wet process has been retrogressive; nevertheless, the unquestioned advantages of the wet process in facilitating intimate mixing of the slurry and the correct proportioning and control of the ingredients has so far generally outweighed other considerations as to render the dry process obsolescent. With the advent of the wet process, fuel consumption so far increased that in kilns of stated fuel capacity the reduction in output (with the old methods of slurry feed) can be taken to be at least 10 per cent. to 15 per cent. compared with that on the dry process for the same consumption. It is small wonder therefore that cement manufacturers have been working at least to make good this loss by decreasing the duty of the fuel, by recuperation, and by better methods of heat transference. In the first two categories come the methods of the use of filters for the reduction of the water content of the slurry and the use of waste-heat boilers.

The matter of heat transference is rather more intricate. The evaporation of the water content of slurry and the subsequent clinkering are effected almost entirely by heat transference from gas to liquid and gas to solid. These cases are amongst the most difficult to follow theoretically. It can be shown, however, that better heat transference may be obtained by increasing the velocity or increasing the effective surface. In the cement industry the former may be regarded as nearly constant for each particular size of kiln with fixed fuel capacity. It therefore remains to increase the suitable area of heating surface. This is the underlying principle of all such methods as the use of lifters or chains for turning over the slurry, extra surface of which is thus exposed to the hot gases, and extra solid surface provided to take up heat from the gases and pass it on indirectly.

Such methods are only a partial solution of the problem. The ideal method of heat transference is that automatically obtained between gas and gas or miscible liquid and liquid. As between gas and solids or liquids the nearest approach to this condition of things is to be got by fine sub-division, and the optimum obtainable in cement making is by "atomising" or spraying the slurry into the kiln.

The method of slurry spraying is therefore fundamentally sound, and is, indeed, nearly theoretically perfect for the type of heat transference under consideration. It has remained to develop it in such a way as to render it equally sound in practice, and this has been accomplished by the process evolved by the late Thomas Rigby and brought to a state of mechanical efficiency by the inventor and his associates.

The process and its method of use are being developed by Messrs. Industrial

Driers, Ltd., of London. Remarkable results have been achieved by the Rigby process, and, with earlier mechanical difficulties overcome, the process is being increasingly adopted throughout the world.

The underlying features of the Rigby process are: (a) the spraying of the slurry down the length of the kiln in counterflow to the ascending hot gases; (b) the use of directional control of the spray so that the evaporation is so far completed before the slurry touches the walls that there is little or no adherence, and therefore a reduced tendency to build up slurry rings; and (c) the use of a slurry lute in the smoke chamber for the collection of dried or partially dried slurry deposited from the spray or carried over from the kiln.

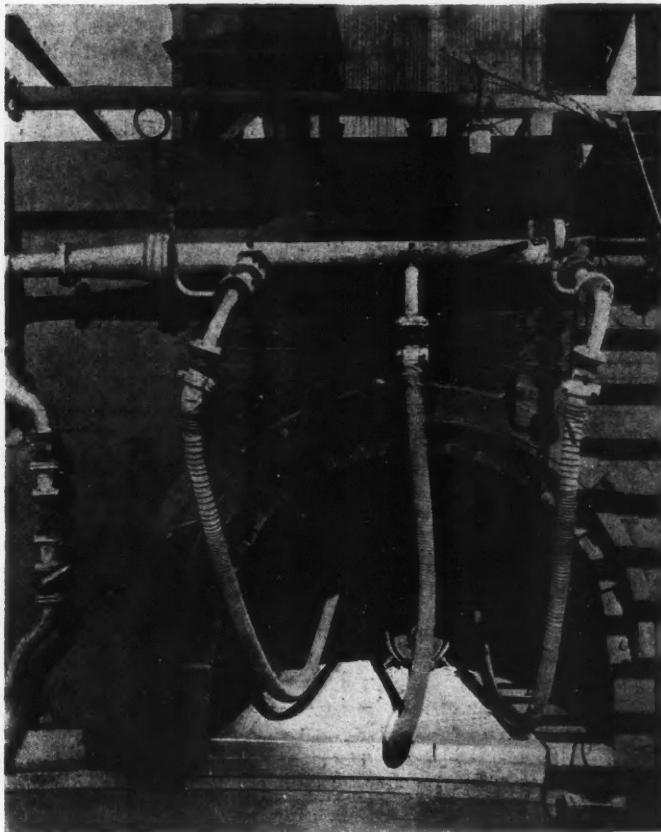
Not only is the trouble from slurry rings minimised and in most cases entirely obviated, but the dry meal and the clinker are generally of smaller size than those produced from the same materials by part methods, the clinker at one works on test with the process being reduced to a coarse powder with about 80 per cent. capable of passing an 1/8-inch screen.

The process can be varied slightly according to the nature of the slurry and the size of the kiln, but as a rule two cones of spray are produced, the direction of which can be adjusted and the relative pressure modified so as to give interlacing zones distributed along the kiln, thus effectively interposing a double barrage of slurry spray across the path of the hot gases. When a single spray is used it is adjusted, as regards spread and distance from the kiln-mouth, to produce as effective a spray screen as possible. When the double spray is employed the pressure on one jet is kept around 70 lbs. per square inch and the other at a few pounds less. By these means the most intimate contact is obtained between slurry and hot gases, and evaporation proceeds efficiently. At the same time the slurry spray arrests and washes down dust which would otherwise be carried out through the stack, and in this way mitigates the dust nuisance.

In practice the slurry is passed through a Clarke separator or similar device to ensure efficient removal of large particles which might interfere with the proper flow of the slurry or the shape and direction of the sprays. The cleaned slurry is then delivered by suitable pumps through strong flex to the nozzles. Ram pumps are generally used for the purpose, but there is no reason why centrifugal pumps should not be employed, and in one or two works where the process has been recently installed this is being done with good results.

Experience has shown that the feed pressure is best hand-governed by a pressure-control valve, excess slurry being returned either to the feed tank or the main slurry tank. The nozzles are mounted in a steel plate forming part of a housing projecting from the anterior wall of the smoke chamber, the slurry being sprayed as a rule across a part of the passage conveying the gases from the cold end of the kiln. The nozzles are of simple construction without moving parts and require very little attention, the only parts which wear out being the tips and to a lesser extent the spiral guides which may be employed to give direction and a rotary motion to the spray.

The nozzle tips can be made of various materials. Mild steel, case hardened, is largely used and this lasts on an average 70 hours. White cast iron is also extensively employed, particularly on the Continent where it is regarded more favourably than case-hardened mild steel, and such tips are claimed by several works to last 100 to 120 hours. In the United Kingdom one firm uses a specially hard proprietary steel, and these tips last at least 300 hours. The cost of the tips is inconsiderable and replacement can be made in a minute or two, so that there is no stoppage of the kiln or interference with output. The tips are replaced, or may be bushed, when observation indicates that wear has proceeded sufficiently to cause the spray to waver in its course when issuing



Spray Feed Installation at a Modern Factory.

from the jet. The spiral guides need only be replaced every two or three months, and other parts of the nozzle last indefinitely.

The chief advantages of the Rigby spray-feed process are claimed to be increased output or decreased fuel consumption, or both, and it is on this basis that claims for its revolutionary character are based. The actual extent of fuel economy or increased output depends on such factors as the nature and the water-content of the slurry, the calorific value and efficiency of combustion of the fuel, the size and nature of construction of the kiln, etc. Estimation of the benefit to be anticipated can therefore only be made for each individual case as a result of consideration of the existing conditions of operation.

In practice the reduction in coal consumption, calculated per unit weight of cement, varies as a rule from 15 per cent. to 20 per cent., and the increased output per kiln from 20 per cent. to 30 per cent. In the following cases, taken from a list of works operating the process, the results achieved have been as follows :—

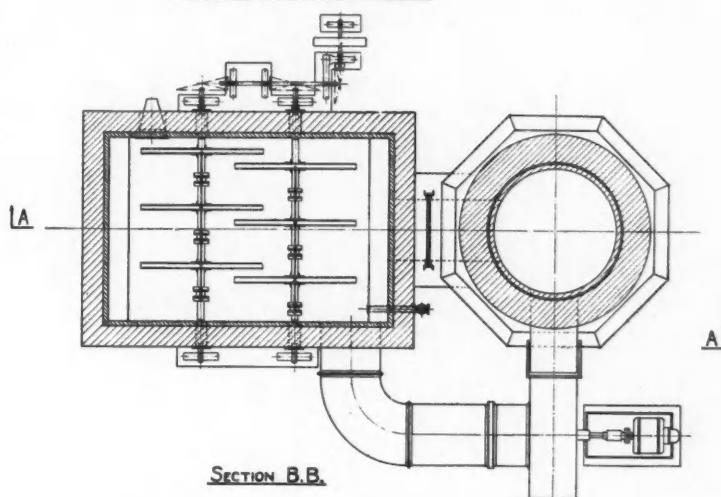
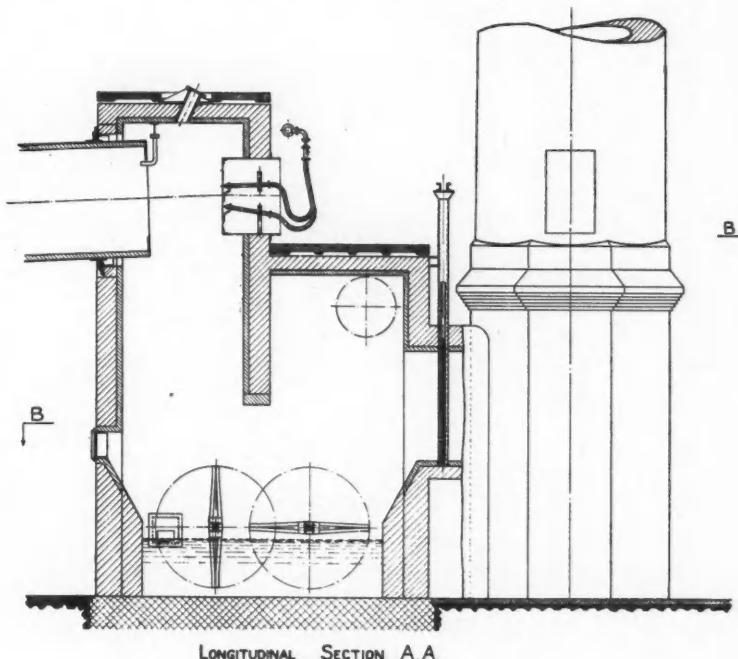
| Works. | Country. | Water content | Reduction of | Increased output |
|--------|----------------|---------------|-------------------|------------------|
| | | of slurry. | fuel consumption. | per kiln. |
| A | United Kingdom | 40 | 20 | 25 to 30 |
| B | Belgium | 42-43 | 20 | 25 |
| C | Scandinavia | 38 | — | 23 to 27 |
| D | Poland | 37 | — | 25 |
| E | Australia | 40 | — | 19 |

These results support the claims made for the outstanding nature of the spray process. Further, the operating and maintenance costs are low and do not appreciably affect the net saving. As regards maintenance, the only working parts likely to suffer wear apart from ordinary depreciation are the nozzle tips and guides already mentioned, and the slow wear from abrasion of the perforated separator plates and pump packings, the cost of replacement of which is negligible. The total maintenance costs are stated to be less than one-twentieth of a penny per barrel of cement.

It is not necessary to employ extra labour, the kiln men being capable of operating the process as part of their routine. It is, of course, advantageous to put control of the atomising in the hands of one man, who, however, can perform other duties.

In the case of new plants the capital cost is inconsiderable. For existing plants the modification of the smoke chamber forms the largest outlay, consisting of minor structural alterations to permit of the installation of the spraying assembly and the deflection of the kiln gases over the slurry lute, and the installation of a fan to make up for the loss of draught occasioned by the cooling of the exit gases in the spray process. The cost of structural alteration varies with each installation, but is seldom more than a few hundred pounds. This, of course, does not include new plant, i.e. atomising and paddle gear, fan, and motor.

The size of the fan is calculated for each individual case, but it should be pointed out that the fan duty is to make up for the drop in temperature, there



Arrangement of Spray Slurry Device for Rotary Kiln.

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being little or no resistance from the spray to the flow of gases. Powerful fans such as are used for waste-heat boilers are not needed. The temperature of the exit gases measured at the entrance to the smoke chamber is considerably reduced by the spray process, generally by 200 deg. C. to 250 deg. C., but owing to the difficulty of obtaining strictly comparable observations the actual temperature is not a good criterion of the efficiency of operation.

The slurry lute, which is an important feature of the Industrial Driers spray installations, is also covered by world-wide patents. It consists essentially of a volume of slurry in the bottom of the smoke chamber, kept agitated by paddles set in counter rotation, and combined with means for the deflection of the kiln exit gases over its surface. By this means all deposits from the jets and any dust carried away from the kiln are washed down into the slurry, which passes continually over a constant-level weir and is thence conveyed to the slurry tank or direct to the kiln for re-use.

The slurry lute is of particular value when powdery raw materials are employed. It practically eliminates the dust trouble arising from the use of rotary kilns, and as such is of vital importance in reducing loss and ameliorating conditions where accumulation of flue dust or its distribution over the neighbouring country constitutes a nuisance. In very severe cases arrangements are also made for spraying slurry into the smoke chamber, but it is only in rare instances that this added washing has been found necessary.

On this basis it is possible to sum up the power consumption for an average works using the spray process, though it will naturally vary with the size of the plant. About 15 H.P. is required for the ram pumps, 6 H.P. for the paddles, 15 H.P. for the fan, and 2 H.P. for the separator when used. With power at one halfpenny per unit the total operating and maintenance charges come well under 2d. per ton. The saving in fuel alone is very considerable. The reduction of operating costs has in itself been sufficient to induce certain cement manufacturers to make the change, whilst to others the chief attraction has been the possibility of increasing output with limited expenditure since it is possible readily to modernise existing rotary kilns by the use of this method. In new works designed for a given capacity the length of the kiln could be considerably shorter with the atomising process than with the older feed methods. This not only lowers capital charges by reducing the length and height of the kiln houses, but effects saving in the power required for rotating the kiln. On an average kiln it is claimed the length could be reduced by approximately 20 per cent.

As compared with the use of chains alone the spraying process is claimed to give much better heat transference and to allay the dust trouble.

A great additional advantage to the spray process is the reduced wear on the kiln lining. In one case the life of the kiln lining has been increased over five times by its introduction, and this saving alone is regarded as sufficient to repay the cost of installation.

The illustrations show respectively a diagrammatic lay-out of a spray installation and a photograph taken from modern works where all three kilns are working with the Rigby spray feed process.

Electrical Equipment of Cranes.

THE most commonly used type of crane is the fixed machine, which has a revolving motion with either a fixed or variable radius, and under the heading of fixed cranes we must include hoists, pulley blocks, jib cranes, and wall cranes. The electric travelling-crane will be dealt with later.

The simplest form of fixed crane is the wall-jib type, having a lifting and slewing motion on a fixed radius. This crane operates on a top and bottom pivot, and can only work within the area of its radius of action; and while cheaper in first cost its application is restricted. The luffing crane, which is the next step in jib cranes, is fitted with a luffing gear in addition to the hoisting gear, which gives the jib a variable radius. A still further development is the level luffing crane, which has found favour for loading and unloading at railway sidings and in large yards, on account of its combined rapid hoisting and luffing motions with small consumption of power. This type of crane is invariably mounted on a carriage or gantry suitable for travelling along the rails at a quayside or railway siding. Another type of electric crane is the mobile crane designed to convey material which is too heavy to be man-handled from one point to another in the factory. An example of this type of crane has a capacity of 2 tons at a 10 ft. 6 in. radius, and 25 cwt.s. at the maximum radius of 15 ft. The propelling motion for the crane is obtained by means of two independent electric motors of the series-wound totally-enclosed type, each of which is connected by gearing to the respective wheels of the castor. The motors are connected in series, and owing to the articulation of the castor axle the load is equally borne on the two wheels, and consequently the torque exerted is the same for each. Independent electric motors operate the hoisting and derricking motions, and automatic self-sustaining electric brakes are fitted. Power is generated by a 20-b.h.p. petrol engine direct-coupled to a 9.50-kW dynamo generating direct current at 250 volts when running at 1,800 r.p.m. The system of control is particularly ingenious and fool-proof, and in order to prevent overwinding on the hoisting and derricking motions a system of limit switches is provided. Means are also provided whereby the crane jib can be depressed, allowing the whole machine to pass under a doorway 10 ft. high by 5 ft. 6 in. wide. The crane can be used anywhere where an ordinary lorry can go, and by running it alongside a truck it can be used to lift goods out of it and transfer them to another vehicle.

Electrical Equipment.

In considering the electrical equipment of cranes, we have to bear in mind (1) the most suitable type of motor to employ and its characteristics in relation to the work to be performed; and (2) the selection of proper control gear. The question of the selection of the most suitable type of motor must first be governed by the system of electrical supply available. If a choice of supply is available, then the direct-current system is most favoured owing to its greater flexibility of control and higher operating efficiency, but this, of course, does not mean that cranes cannot be operated on the alternating-current system.

Dealing with direct-current motors first, the choice lies between the series-wound, shunt-wound, and compound-wound, and of these three the series-wound machine is undoubtedly the most suitable, both on account of its high starting torque and its automatic speed variation. As the starting torque of cranes is high, a motor is called for that will exert a powerful torque at starting from rest, and this is really the outstanding characteristic of the series-wound motor. Instead of varying directly with the current, as in the case of the shunt-wound machine, the torque increases practically with the square of the current; that is to say, if the current is doubled the torque is increased nearly four

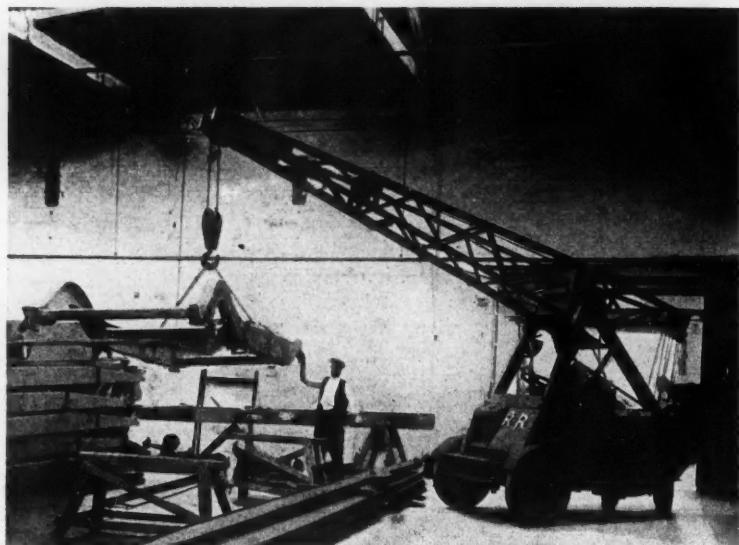


Fig. 1.—Mobile Crane.

times. This particular characteristic of the series motor is due to the fact that when a series-wound machine is switched on the whole of the current flows through both field coils and armature, the effect in the field being to bring the magnetic strength to practically its full amount; thus the torque (the product of magnetic strength and armature strength) will be a maximum for that particular current value.

A further feature which makes this type of motor suitable for crane work is its speed characteristics. The greater the load the less the speed of the motor; the lighter the load the more the motor speeds up. In the event of the load being taken completely off the armature will "run away," and for this reason braking is fitted to the hoisting unit in order to limit the downward speed.

Alternating Current Operation.

Where the supply is on the alternating-current system the choice of motors lies with the slip-ring induction-type motor with a starting torque of at least 2.5 the full load torque. Although the speed characteristics of this machine are not perhaps equal to those of the series motor, the slip-ring motor, by reason of the absence of a commutator, stands up to more severe conditions than the D.C. motor, and, generally speaking, is simpler in construction. The slip-ring motor, in order to obtain a higher starting torque, differs from the squirrel-cage machine by the provision of a more elaborate rotor winding, and the ends of the insulated coils are connected to slip rings placed outside the bearing on an extension of the shaft. The use of these slip rings provides a means of intro-

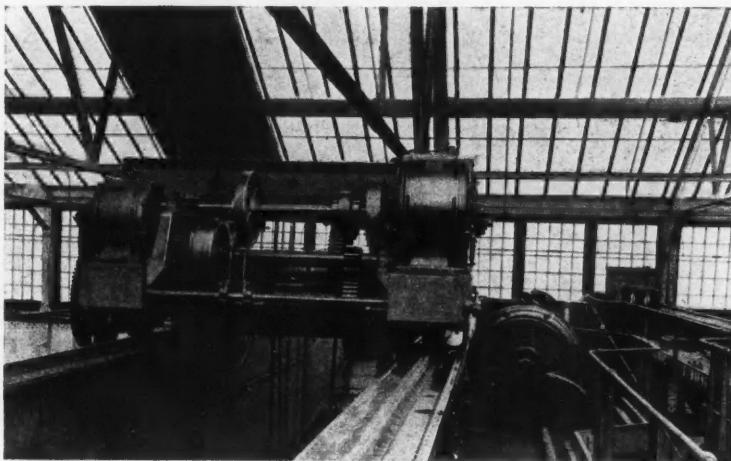


Fig. 2.—Squirrel-Cage Motors Operating a 50-Ton Crane.

ducing resistance on starting into the rotor circuit, increasing starting torque and reducing starting current.

Hitherto the squirrel-cage induction-type motor has been looked upon as quite unsuitable for crane work owing to the excessive amount of current it takes when starting against a reasonable load. Moreover, it possesses a somewhat low power factor; acceleration is poor, and close inching difficult. These disadvantages, however, have now been overcome, with the result that there have been placed on the market at least two types of squirrel-cage motors designed to overcome these drawbacks and calculated to stand up to the slip-ring motor. In the first of these new machines the manufacturers claim a starting efficiency from the point of view of torque and k.v.a. of approximately 75 per cent. better than that of a standard motor, with a power factor of the starting current correspondingly higher. The other machine is claimed to be capable of performing

duties which have hitherto not been possible with squirrel-cage motors, and has been designed so that stopping and starting are carried out by means of a triple-pole switch, no other form of starter being necessary. It is capable of being started, stopped, and reversed under full load from temperature rise, and has very smooth acceleration.

Protection for Crane Motors.

A factor to be borne in mind in the choice of motors, whether A.C. or D.C., is the protection required for crane work, and to this end the totally-enclosed

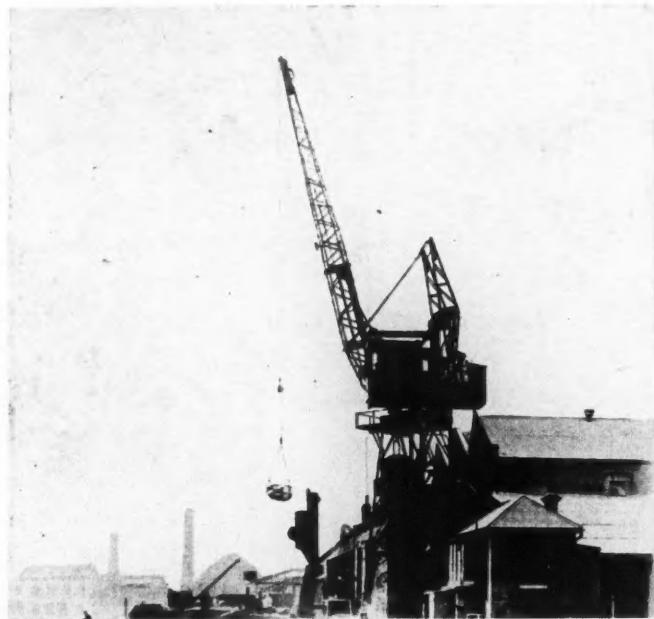


Fig. 3.—Crane Equipped with "Maxtorq" Motors
Handling Cement on a Thames-side Wharf.

machine is usually adopted. Local conditions naturally have a bearing on this subject, and it may be that where the atmosphere is comparatively dry and free from dust and damp the enclosed ventilated-type motor may be used. On the other hand, if the crane is for outdoor use and no covering is provided for the motors then the weather-proof type would be installed. Rating and temperature rise should be governed by the British Engineering Standards Association Regulations.

To determine the horse power of the motor required to drive hoisting mechanism a convenient rule is : H.P. = $\frac{\text{foot tons per minute}}{10}$, while to calculate

the power required to travel a crane, a tractive force of about 60 lb. per ton is usually taken for cranes operating in sheltered positions. For outdoor work the effect of wind pressure must be taken into consideration.

Control Equipment.

As in the case of all other electrically-operated machinery the efficient operation of the crane depends on the control gear, and very careful attention must be paid to this section of the equipment. The duties it has to perform are severe, and only the most robust apparatus will give satisfactory service.

The most usual type in use is the "drum" type controller. The resistances are usually of grid construction, but in some of the small units a wire wound resistance is more suitable. There should be ample room inside the controller for connections, all parts should be accessible, finger tips and drum contacts easily renewable, mica insulation, and a definite step should be felt as the barrel is moved round to each contact. With direct-current controllers a magnetic blow-out should be fitted.

For use with drum controllers, auxiliary apparatus such as resistances, brake solenoids, limit switches, etc., are usually employed, and as drum controllers themselves give no protection against overloads or other risks that may be incurred the installation of additional protective apparatus is essential.

For alternating current shunt solenoids are supplied, and for direct current circuits either series or shunt-wound solenoids are available. In general, except for small motors, series solenoids should be used where possible; having fewer turns of heavier wire they tend to be more robust than the shunt solenoid, besides avoiding the slightly sluggish action caused by the induction of the latter. Shunt solenoids, however, must be used under certain conditions, such as for small motors where rheostatic braking is employed, and under conditions of variable load where the load is liable to fall to a point where the current is reduced to a low value that is insufficient to hold up the brake.

Wiring for crane work should preferably be carried out on the steel conduit system, and conform to the rules of the Institution of Electrical Engineers.

Fig. 1 shows a mobile crane supplied by Messrs. Ransome & Rapier, Ltd.; Fig. 2, squirrel-cage motors supplied by the Metropolitan-Vickers Electrical Co., Ltd., operating a 50-ton crane; Fig. 3, a crane equipped with "Maxtorq" motors supplied by the Lancashire Dynamo & Motor Co., Ltd.

Notes from Abroad.

Developments in Spain.

Compania General de Asfaltos y Portland Asland has increased its capital by 5 million pesetas (£150,200). A Royal Decree has been issued consenting to arrangements being made for the enlarging of the Spanish cement production to the extent of 975,000 tons per annum; this will bring the yearly production up to about 2½ million tons.

South African Tariffs.

The local Board of Trade and Industries has recommended that all existing "dumping" duties on cement should be withdrawn, and that in their place the customs duty be raised from 1s. 3d. to 2s. 6d. per 400 lbs. The present duty is 1s. 6d. per 400 lbs., plus a "dumping" duty which fluctuates according to the difference between home consumption prices and the selling price of the country of origin.

An Australian Merger.

The Kandos Cement Co., Ltd., and Australian Cement, Ltd., are amalgamating their interests. It is proposed either to form a new company to take over these two concerns or to form a third "holding" company, and it is hoped thereby to eliminate inter-state competition and reduce working expenses. Both companies have maintained a 10 per cent. dividend for several years, but the latter company's profits have been steadily declining. The combined capacity of the two companies will be 575,000 tons, which is about 50 per cent. of the total Australian output.

German Cement Exports.

The improvement in the German cement export trade in April slackened off in May. Exports for May at 849,000 tons only slightly exceeded those of April (816,000 tons). The increase of 92,000 tons as compared with May, 1928, has only slightly mitigated the decrease of exports, as the sales in the first five months of the current year in comparison with the same period of 1928 are still 583,000 tons less.

New Plant for Damascus.

We understand that the new plant at Damascus for the Soc. de Ciment Libanais, of Tripoli, is to be commenced early in 1930. The plant is being equipped by the German firm of Mühlenbau und Industrie Aktiengesellschaft, of Braunschweig. The factory, which will have a daily output of 170 tons, is situated by the sea. The raw material, lime and marl, are found in the neighbourhood. Coal and gypsum are to be imported. The marl will be mixed in a mill 1.8 x 10 m. The dimensions of the rotary kiln are 2.8 x 60 m., fitted with coolers. Packing will be by a modern electric Miag packer, and the cement will be principally transported direct to ships by means of a conveyor. Power for the plant will be produced at the works' own generating station, while it is anticipated that the heat from the kiln will be utilised later.

The Reactions in Burning Cement.

By A. G. DAVIS, M.I.Mech.E., M.Inst.C.E.I., F.C.S.

(*Works Managing Director, Associated Portland Cement Manufacturers, Ltd.*)

CEMENT clinker is usually produced by heating together a mixture of limestone or chalk and clay, until the material sinters. After the expulsion of the carbon dioxide from the limestone and of the combined water and organic matter from the clay—processes which may be regarded as completed at 1,100 deg. C. (2,012 deg. F.)—the lime, alumina, and silica unite between 1,100 deg. C. and 1,500 deg. C. (2,012 deg. F. and 2,732 deg. F.) and ultimately produce the mixture of calcium silicates and aluminates which composes Portland cement clinker.

Heat is evolved during the process of combination, but the exact amount is a matter of dispute.

It is generally agreed that the dehydration of the aluminium silicate in the clay requires the expenditure of some energy, but the amount is not accurately known; also, that the reaction of the lime (liberated by the decomposition of the calcium carbonate) on the silica and alumina of the clay to form calcium silicates and aluminates is probably exothermic and supplies a small amount of heat. It is accepted by authorities that these plus and minus quantities may be regarded as balancing each other without serious error.

The first writer to take into account the exothermic reaction of clinker formation in calculations relating to the efficiency of the rotary kiln was Joseph W. Richards in 1904. He worked out experimentally a complete heat balance for a 60-ft. rotary cement kiln, and fully discussed the influence thereon of the exothermic reaction of clinker formation. Richards' comments are: "The combination of the ingredients of the clinker evolves a large quantity of heat, equal to 18 per cent. of the heat developed by the combustion of the coal. This quantity is surprisingly great, but is a reality from the chemical standpoint." Richards concludes as follows: "An extremely interesting fact is here brought out, viz. that the clinker leaving the kiln at 1,200 deg. C. (2193 deg. F.) is hotter than the mixture of gases in the kiln. It is its heat of combination which causes this, and which accounts for the anomaly. In fact, the heat of combination probably heats the clinker even hotter than 1,200 deg. C. in the interior of the kiln."

Le Chatelier comments on Richards' remarks as follows: "The heat of combination of silica and alumina with lime is not properly known. I have made some measurements on the formation of calcium monosilicate, $\text{CaO} \cdot \text{SiO}_2$, and it is these figures, reproduced inexactly in different publications, which have served as a starting point for Mr. Richards' calculations. As a matter of fact these figures lead to a value less than half of those given by Mr. Richards."

E. C. Soper published in 1905 details of a complete test of the thermal efficiency of a 100-ft. rotary cement kiln. In this complete and elaborate research allowance is made for the exothermic reaction of clinker formation.

According to Soper, in the clinker from 248.64 lbs. of CaO per barrel of cement (380 lbs.) there were liberated 237,164 B.T.U.'s, and from the 3.4 lbs. of MgO per barrel of cement there were liberated 5,061 B.T.U.'s, making a total of 242,225 B.T.U.'s per barrel of cement.

In 1905, in spite of this work, much doubt still existed as regards the reality or otherwise of the exothermic reaction of clinker formation. For example, Richard K. Meade thus refers to the matter: "The combination of the lime with the silica and alumina is also thought to be an exothermic reaction, but authorities differ on this point. . . . It is the one stumbling block to our calculating the efficiency of the rotary kiln. It seems probable that the reaction does give off some heat, though the amount is very small."

In the same year Henry S. Spackman, in an address to the American Portland Cement Manufacturers' Association, said: "In general it is assumed that heat is liberated (during the sintering process) but experiments, not yet completed, in my laboratory show that this reaction is only weakly exothermic or probably endothermic." Spackman apparently never published details of these experiments.

Timm in 1906 remarked as follows: "Richards and Naske have recently put forward the view that the sintering of cement proceeds exothermically, and on that account consider that the sintering zone is too short in comparison with the CO₂ zone. In the first place, this conclusion was due to an erroneous gas analysis, and in the second place the strong exothermic reaction assumed by Richards and Naske does not agree with Le Chatelier's work, which was based on a study of certain constituents of cement. Observations on other cement kilns show that at most there is only a very small exothermic reaction, and my own calculations confirm this. An immediate consequence of a strong exothermic reaction would be the development of a process of burning such that if the raw materials were placed in a chamber and heated to 1,175 deg. C. (2,147 deg. F.) by means of grate-firing, and were then played upon at one point with a blowpipe flame, the entire mass would spontaneously ignite and its temperature would increase to 1,450 deg. C. (2,642 deg. F.)!"

The Russian authority Tschernobaeff investigated experimentally the heat of formation of certain silicates and aluminates by a method which had previously been applied by Le Chatelier, consisting in placing a mixture of charcoal, silica, and a compound of the base to be studied in the oxygen bomb-calorimeter. On ignition the heat developed by the combustion of the charcoal in the oxygen caused the silica to unite with the salt to form the silicate required. Tschernobaeff's work was published in 1905, with details of the methods used for making the necessary corrections.

In 1912, however, Tschernobaeff and Wologdine repeated their experiments on the heat of formation of the calcium silicates and obtained somewhat different results. Tschernobaeff also determined the heat required to remove the combined water from clay (kaolin). He obtained the value: (Al₂Si₂O₇, 2H₂O) = 28,900 gram calories.

J. W. Mellor and A. D. Holdcroft, repeating Le Chatelier's experiments, com-

puted the heat of dehydration of kaolin by means of heating curves and obtained the results $H_4Al_2Si_2O_9 = 2H_2O + Al_2O_3 \cdot 2SiO_2 - 10,800$ g. calor. This is little more than a third of the value obtained by Tschernobaeff. In other words, in order to dehydrate clay (kaolin) the following quantities of heat and coal are required:

HEAT REQUIRED TO DEHYDRATE CLAY.

| | Tschernobaeff (bomb calorimeter). | Mellor and Holdcroft (heating curves). |
|--------------------------|--|---|
| Per kilogram kaolin ... | 112 kilo calories | 41.9 kilo calories |
| Per lb. ... | 202 B.T.U.'s | 75.5 B.T.U.'s |
| Per ton ... | 452,500 B.T.U.'s (0.0160 ton coal) | 169,100 B.T.U.'s (0.00598 ton coal) |
| Per 100 tons clinker ... | 12,450,000 B.T.U.'s (0.44 ton coal) | 4,650,000 B.T.U.'s (0.164 ton coal) |

The last result is worked out on the basis that 100 tons of clinker require 27.5 tons of dry clay (assumed pure kaolin, which is not correct, but represents a maximum value) and that 1 lb. of coal liberates 12,600 B.T.U.'s when burnt.

According to Mellor and Holdcroft the main heat absorption took place between 506 deg. C. (932 deg. F.) and 750 deg. C. (1,382 deg. F.). It is difficult, however, to obtain accurate numerical values by the heat curve method as so many unknown quantities enter into the computation.

Mellor and Holdcroft deduce from their heating curves that when kaolin is heated there result:

(1) Endothermic decomposition, near 500 deg. C. (932 deg. F.), in all probability corresponding with the formation of free silica, free alumina, and water.

(2) An exothermic change, near 800 deg. C. (1,472 deg. F.), probably corresponding with the polymerisation of the alumina.

(3) An exothermic change, near 1,200 deg. C. (2,192 deg. F.), probably corresponding with the recombination of silica and alumina formed in the vicinity of 500 deg. C. (932 deg. F.).

Mr. Satch repeated this work with Japanese kaolin and confirmed (1) an endothermic reaction between 470 deg. C. (878 deg. F.) and 700 deg. C. (1,292 deg. F.); (2) an exothermic reaction at 950 deg. C. (1,742 deg. F.); (3) an exothermic change between 1,200 deg. and 1,300 deg. C. (2,372 deg. F.). He gives no numerical values for the magnitude of the heat quantities involved.

It will be seen that the assumption of other authorities regarding the heat required for dehydration of clay and combination of the lime and silica requires to be reconsidered in the light of these researches.

Otto Dormann in 1914 used Tschernobaeff's 1905 results in order to calculate the exothermic reaction of clinker formation as follows: He assumes that a normal Portland cement clinker consists of 77.5 per cent. of calcium silicates and 22.5 per cent. of calcium aluminates and ferrites. The heat absorbed by

the formation of 1 kilogram of tri-calcium aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (from the component oxides) is small and can be neglected. Similarly the heat evolved from the formation of the ferrites in the clinker is negligible, seeing that they form so small a proportion of the mass. It is therefore only necessary to consider the heat evolved by the formation of the 77.5 per cent. of calcium silicates in the clinker.

Dormann assumes that the calcium silicate content of Portland cement clinker is a mixture of dicalcium and tricalcium silicates in equal weights (2.5 CaO. SiO_2), so that the heat of formation of 1 kilogram of this mixture of silicates is $\frac{1}{2}(125 + 165) = 145$ kilo calories per kilogram. Hence the heat produced by the formation of 77.5 kilograms of the silicates is $77.5 \times 145 = 11,240$ kilo calories, i.e. 100 kilograms of clinker evolve this amount of heat when formed. Helbig recalculated these results and gives 11,240 kilo calories as the approximate and 11,400 kilo calories as the more exact heat of formation of 100 kilograms of clinker. Dormann accepts this value as the more correct one.

In an earlier treatise Dormann pointed out the importance of the exothermic reaction in the theory of the rotary kiln and made the following remarks on the subject: "The action once started proceeds of itself; the heating up of the clinker does not proceed gradually from 1,100 deg. C. to 1,350 deg. C. or 1,500 deg. C. (2,012 deg. F. to 2,462 deg. F. or 2,732 deg. F.), but the reaction takes place suddenly and completely of itself within a moment, as can be verified by the optical pyrometer."

In a later paper the same author says the last trace of carbon dioxide is only expelled at 1,100 deg. C. (2,012 deg. F.). Hence it is only when the raw material reaches this temperature that it becomes capable of forming clinker. The sintering reaction then abruptly begins; the temperature of the raw mass suddenly rises to 1,500 deg. C. (2,732 deg. F.). Sintering, however, will only occur if the raw mass is extremely finely divided so as to be capable of rapid and complete chemical interaction, and possesses a composition which allows the formation of 77.5 parts of calcium silicates and 22.5 parts of calcium aluminates and ferrites. Under these conditions, 100 kgm. of clinker thus produced will evolve 11,400 kilo calories—a quantity of heat capable of raising the temperature of the raw mass from 1,100 deg. C. to 1,643 deg. C. (2,012 deg. F. to 2,990 deg. F.). Dormann asserts that the latter temperature is never reached in practice owing to losses of heat by radiation and conduction. The optical pyrometer gives the surface temperature of the clinker as 1,550 deg. C. (2,822 deg. F.). "It follows from this," he says, "that the sintering of cement does not require so extremely high a degree of heat as is usually asserted. The great thing to do is properly to prepare the raw meal so that when the action has once started it proceeds by itself to completion."

Dormann finally suggests that it is not only the total number of calories yielded from coal, but also the capacity of the coal to burn sufficiently rapidly to generate a high temperature, that is the best criterion of its technical value for cement production.

In 1920 R. R. Coghlan published a paper in which he calculates the exothermic reaction of clinker formation along the same lines as Dormann. Coghlan used a raw material consisting of

| | | | | | |
|-----------------|---|-----|-----|-----|--------------------------------------|
| Clay | $\left\{ \begin{array}{l} \text{Al}_2\text{O}_3 \text{ 25.57 lbs.} \\ \text{SiO}_2 \text{ 87.59 lbs.} \\ \text{Fe}_2\text{O}_3 \text{ 10.92 lbs.} \end{array} \right\}$ | ... | ... | ... | 124.08 lbs. = 21.53 per cent. |
| CaCO_3 | ... | ... | ... | ... | 436.43 lbs. = 75.74 per cent. |
| MgCO_3 | ... | ... | ... | ... | 15.76 lbs. = 2.73 per cent. |
| | | | | | <hr/> 576.27 lbs. = 100.00 per cent. |

When calcined this produced 376 lbs. of clinker, to which he ascribes the composition :—

| | | | |
|----------------------|-----|---|-------------------|
| Tricalcium ferrite | ... | $3\text{CaO} \cdot \text{Fe}_2\text{O}_3$ | 22.38 lbs. |
| Tricalcium aluminate | ... | $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ | 67.65 lbs. |
| Tricalcium silicate | ... | $3\text{CaO} \cdot \text{SiO}_2$ | 111.47 lbs. |
| Dicalcium silicate | ... | $2\text{CaO} \cdot \text{SiO}_2$ | 166.98 lbs. |
| | | | <hr/> 368.48 lbs. |

" This composition is arrived at by calculating all iron oxide and alumina to the tricalcium compounds, and taking the balance of the lime and apportioning it between the silica as tri- and di-calcium silicates on the basis of the percentage composition."

Now according to Tschernobaeff's 1905 results :

- 1 lb. of tricalcium silicate evolves on formation 225 B.T.U.'s
- 1 lb. of dicalcium silicate evolves on formation 297 B.T.U.'s
- 1 lb. of tricalcium aluminate absorbs on formation 47 B.T.U.'s

The heat of production of ferrites is so small as to be negligible. Hence we have for heat evolved on formation of clinker :—

| | Weight. | B.T.U.'s evolved on formation. |
|----------------------|---------|-----------------------------------|
| Tricalcium silicate | ... | 111.47 lbs. + 25,080 |
| Dicalcium silicate | ... | 166.98 lbs. + 49,600 |
| Tricalcium aluminate | ... | 67.65 lbs. - 3,180 |
| Tricalcium ferrites | ... | 22.38 lbs. — |
| | | <hr/> 368.48 lbs. 71,500 B.T.U.'s |

For 368.48 lbs. of clinker produced there are evolved + 71,500 B.T.U.'s (Coghlan's value was 70,496 B.T.U.'s).

Re-calculation of these results on Tschernobaeff's 1905 data to B.T.U.'s per 100 tons in the usual manner gives the following:

| | | |
|---|-----|---------------------|
| B.T.U.'s evolved per 100 tons of clinker produced | ... | 43,465,000 B.T.U.'s |
| Equivalent in tons of coal (of 12,600 B.T.U.'s per lb.) | | |
| per 100 tons of clinker produced | ... | 1,576 tons |

| | | |
|---|-----|-----------------------|
| Kilo calories evolved per 100 kilograms of clinker produced | ... | 10,780 kilo calories. |
|---|-----|-----------------------|

On recalculation of Coghlan's results on the basis of Tschernobaeff's and Wologdine's 1912 data, we obtain the following value for the exothermic reaction of clinker:

| | | |
|---|-----|---------------------|
| B.T.U.'s evolved per 100 tons of clinker produced | ... | 39,977,000 B.T.U.'s |
| Equivalent in tons of coal (of 12,600 B.T.U.'s per lb.) | | |
| per 100 tons of clinker produced | ... | 1,416 tons |

| | | |
|---|-----|----------------------|
| Kilo calories evolved per 100 kilograms of clinker produced | ... | 9,916 kilo calories. |
|---|-----|----------------------|

Coghlan then proves experimentally that an exothermic reaction does occur, as follows: "The foregoing clinker was made in an electric furnace. Starting with the furnace temperature at 2,000 deg. F. (1,093 deg. C.) and the raw mixture cold it was found that exactly 37 minutes were required to produce clinker from this mixture. The temperature, which was observed by a Leeds and Northrup pyrometer, was found to rise steadily to 2,360 deg. F. (1,293 deg. C.) when it took an instantaneous rise to 2,438 deg. F. (1,337 deg. C.). Here it remained stationary and the clinker was then withdrawn from the furnace and found to be perfectly fused. This phenomenon was observed each time the mix was burnt."

Coghlan estimates the latent heat of fusion of clinker to be in the neighbourhood of 10.25 B.T.U.'s per lb. of clinker, i.e. 2,296,000 B.T.U.'s or 0.0814 ton of coal (12,600 B.T.U.'s per lb.) per 100 tons of clinker, or 569.5 kilo calories per 100 kilograms of clinker.

In 1911 Tschernobaeff again attacked the problem and determined directly the heat of formation of Portland cement clinker by the same method as that previously used. He came to the conclusion that the formation of clinker is accompanied by the development of very considerable quantities of heat; calculating on 1 gram of CaCO_3 he found that the heat evolved diminishes according as the " basicity " (hydraulic modulus) of the raw mass increases. For cements of ordinary constitution, which are produced from a raw material containing about 75 per cent. CaCO_3 this evolution of heat (after subtracting the heat of dissociation of the CaCO_3) amounts to 115 to 118 gram calories reckoned on 1 gram of CaCO_3 . Tschernobaeff calculated in this manner the total heat of formation of clinker produced under factory conditions at about $+115 - 435 = -320$ gram calories on 1 gram CaCO_3 in the mixture.

Recalculating these results on the basis that an average clinker contains 65 per cent. of CaO we get the following results:

| | | |
|--|-------------|-----------------------------------|
| B.T.U.'s evolved per 100 tons of clinker produced | | 53,830,000 to 55,240,000 B.T.U.'s |
| Equivalent in tons of coal (of 12,600 B.T.U.'s per lb.) per 100 tons of clinker produced | | 1.91 to 1.96 tons |
| Kilo calories evolved per 100 kilograms of clinker produced | | 13,350 to 13,700 kilo calories. |

Meanwhile the subject was being attacked from another point of view. In 1910 E. Dittler introduced a method of "heat curves." A well-known method of ascertaining whether any decomposition or other change occurs in a substance when it is heated consists in heating a little of the substance in a crucible in an electric furnace in such a manner that the temperature of the furnace rises at a perfectly uniform rate. A pyrometer is then placed in the contents of the crucible, and it is found that with many minerals and alloys the temperatures recorded by the pyrometer do not rise regularly but show a "lag" or "rest" at some points of the time-temperature curve, and a sudden rise of temperature (during which the substance becomes hotter than the furnace) at other points. The "lag" is caused by the heat absorbed by the substance being so great that the temperature cannot rise. This is an indication that a heat-absorbing (or endothermic) reaction is occurring, whereas a "lump" or projection in the time-temperature curve of the experiment indicates that the substance is giving out heat, i.e. that an exothermic reaction is taking place.

E. Dittler carried out experiments on these lines by placing a mass of 30 to 40 grams of finely-ground raw material suitable for producing clinker in an electrical Heraeus resistance furnace and steadily heating by a given electric current, the rate at which the temperature of the material increased in comparison with the rate of increase of the furnace being noted. It was found that an endothermic reaction set in at 1,350 deg. C. (2,462 deg. F.) and 1,500 deg. C. (2,732 deg. F.)—the latter being no doubt due to the partial fusion of the substances and absorption of the latent heat of fusion—but at 1,425 deg. C. (2,597 deg. F.) to 1,430 deg. C. (2,606 deg. F.) a strong exothermic reaction occurred. No exact determinations of the amount of heat set free were made.

In 1914 the British Portland Cement Research Association approached the National Physical Laboratory with a view to determining the exothermic reaction of clinkering. The National Physical Laboratory worked on much the same lines as Dittler and Jesser by means of heat curves, but used an optical pyrometer to determine the temperature. Samples of cement raw material slurry and cement were heated up side by side in a small furnace, means being provided for constantly observing independently the temperature of the slurry and of the cement by means of an optical pyrometer. Should heat be liberated during the clinkering process its effect would be shown by a sudden increase in the temperature of the cake of slurry as compared with the temperature of the cake of cement.

In many of the experiments the slurry and cement heated up at the same rate, and no difference of temperature could be detected during the process of clinkering. After numerous trials, however, a certain rate of heating was found during which the slurry warmed up much more rapidly than the cement between the temperatures of 1,100 deg. C. (2,012 deg. F.) and 1,200 deg. C. (2,192 deg. F.), the time occupied between these limits being about one minute. The opinion was expressed that the total heat evolved would not be more than that necessary to raise the temperature of the material by 100 deg. C. (212 deg. F.). This would be sufficient to reduce the coal consumption of the kiln by about one-third of 1 per cent. reckoned on the clinker.

Accepting this admittedly rough estimate as approximately correct, and taking the specific heat of the materials heated as 0.2, the heat required to raise 1 kilogram of material through 100 deg. C. is 20 kilo calories. Hence we deduce the following figures:

| | | |
|---|-----|----------------------|
| B.T.U.'s evolved per 100 tons of clinker produced | ... | 8,064,000 B.T.U.'s |
| Equivalent in tons of coal (of 12,600 B.T.U.'s per lb.) | | |
| per 100 tons of clinker produced | ... | 0.2856 tons |
| Kilo calories evolved per 100 kilograms of clinker produced | ... | 2,000 kilo calories. |

It will be observed that this value is only about one-fifth to one-sixth of that which depends upon Tschernobaeff's bomb-calorimetric method.

E. Janecke, in September, 1914, described cooling curves obtained by heating mixtures of CaO, Al₂O₃ and SiO₂ in a platinum crucible to 1,600 deg. C. (2,912 deg. F.) in an electric furnace, immersing a thermo-element therein and observing the rate of cooling. A sudden evolution of heat occurred at the point 1,381 deg. C. (2,518 deg. F.) corresponding to a composition 8CaO Al₂O₃ 2SiO₂.

In 1921 Dr. K. Endell published an account of heat curves obtained from the mixture of limestone and clay used in the manufacture of Portland cement at Rudersdorf. A steady curve was obtained until a temperature of 930 deg. C. (1,706 deg. F.) was reached, when a lag occurred in the rise of temperature indicating that heat was being absorbed (probably due to the evolution of carbon dioxide from the limestone). The temperature then rose steadily until 1,200 deg. C. (2,192 deg. F.) was reached, when heat was evolved and the temperature rapidly increased to 1,300 deg. C. (2,372 deg. F.).

In 1910 L. Jesser dissolved in hydrochloric acid completely burnt clinker and also slurry heated sufficiently just to expel the carbon dioxide but not to form clinker. On measuring the difference in the heat evolved on solution Jesser came to the conclusion that the conversion into clinker of slurry, from which the CO₂ had already been expelled, was attended with a small absorption of heat. The next to attack the problem along these lines was Professor R. Nacken. Nacken classifies the burning of cement in the following manner:—

- (1) Evolution of combined water of clay, 500 deg. C. (932 deg. F.) endothermic.
- (2) Evolution of CO₂ to 900 deg. C. (1,652 deg. F.) endothermic.

(3) Reaction between CaO and clay, 900 deg. C.-1,200 deg. C. (1,652 deg. F.-2,192 deg. F.) exothermic (formation of Ca silicates and aluminates).

(4) Incipient fusion and continuance of some silicate, etc., formation, 1,250 deg. C. (2,282 deg. F.) endothermic.

Nacken proceeds to check this classification by an improvement upon Jesser's work, with whose results he does not agree. In principle, he takes (*a*) a sample of raw meal heated to about 900 deg. C. so that the CO₂ has been driven off but the reaction between CaO and clay has not commenced, and (*b*) a sample of raw meal heated to a higher temperature so that the CaO-clay reaction has occurred. These two samples are ground and dissolved in a mixed solution of HCl and HF, the rise in temperature being taken by means of a Beckmann thermometer on which readings can be estimated to 1/1,000 deg. C. The difference in the heat values of the two reactions gives the exothermic value of clinker formation.

The apparatus used consists of a calorimeter—a platinum beaker suspended in a copper beaker. The experiments are arranged to reduce corrections to a minimum, and the highest temperature due to the solution is reached in one minute. The temperature/time curves of the calorimeter are plotted. The author uses samples of material taken along the length of a kiln, so that the temperatures of formation and the composition of the samples are known. He finds that the heat of solution increases suddenly as soon as the bulk of CO₂ is driven off and afterwards shows a slow increase with the temperature of formation of the sample. The heat of solution quickly attains a maximum and slightly decreases with temperature of burning, as is to be theoretically expected. The important fact is that the exothermic reaction is essentially completed soon after the removal of CO₂, the further heating to incipient fusion merely serving to give the cement the desired technical properties.

The experiments were repeated on special samples of raw meal, and the value of the exothermic reaction was calculated by comparing the heat value of the sample showing a maximum heat value with that obtained on dissolving a mechanical mixture of CaO, Al₂O₃, Fe₂O₃, and SiO₂ of the same composition. The difference between these two heat values is taken to represent the exothermic reaction, which works out at 100 gram calories per 1 gram of clinker. From this figure the increase of temperature of the burning cement due to the exothermic reaction is calculated to be 25 deg. C. (77 deg. F.), which is in close agreement with the value obtained from heating curves. The heat necessary completely to burn 1 kilogram of clinker is calculated to be 900 kilo calories, i.e. 100 tons of clinker theoretically require for production 362,907,000 B.T.U.'s, or 12.86 tons of coal of 12,600 B.T.U.'s per lb.

From the foregoing data the following is calculated:

B.T.U.'s evolved per 100 tons of clinker produced ... 40,323,000 B.T.U.'s

Equivalent in tons of coal (of 12,600 B.T.U.'s per lb.)

per 100 tons of clinker produced 1.428 tons

Kilo calories evolved per 100 kilograms of clinker

produced 10,000 kilo calories.

It will be seen from the foregoing that four distinct methods have been used

for determining the value of the exothermic reaction of clinker formation. These methods are:

(1) By determining the heat of formation of the component silicates and aluminates which form clinker and calculating therefrom the heat of formation of clinker itself (Richards, Le Chatelier, Dormann, Coghlan).

(2) By direct determination in a bomb calorimeter using charcoal as the source of heat (Tscher nobaeff).

(3) By means of heat curves (Dittler, National Physical Laboratory, Janecke, Endell).

(4) By solution of the raw materials and clinker in acids and measuring the thermal effects involved (Jesser, Nacken).

The following Table I is a summary of the more important determinations.

TABLE I.
Heat Evolved during the Exothermic Reaction of Clinker Formation.

| Authority. | Date. | Equivalent in tons of coal (of 12,600 B.T.U.'s per lb.) per 100 tons clinker. | B.T.U.'s per 100 tons clinker. | Kilo-Calories per 100 kilos clinker. | Method of determination. |
|---------------------|-------|---|--------------------------------|--------------------------------------|---|
| J. W. Richards ... | 1904 | 5.920 | 167,084,000 | 41,430 | Calculated from Berthelot's values for the heat of formation of the calcium silicates. |
| H. Le Chatelier ... | 1905 | 2.651 | 74,860,000 | 18,560 | Calculated from Le Chatelier's values for the heat of formation of calcium silicate. |
| E. C. Soper ... | 1905 | 2.267 | 64,000,000 | 15.870 | Do. Do. |
| D. Tscher nobaeff | 1911 | 1.91 to 1.96 | 53,830,000 to 55,240,000 | 13,350 | Direct determination by burning calcium carbonate and clay to cement in a bomb calorimeter in presence of charcoal as heating agent. |
| O. Dormann ... | 1914 | 1.606 to 1.628 | 44,330,000 to 44,960,000 | 11,240 to 11,400 | Calculated from Tscher nobaeff's 1905 determinations of the heat of formation of the calcium silicates and aluminates. |
| R. Coghlan ... | 1920 | 1.416 | 39,977,000 | 9,916 | Calculated from Tscher nobaeff's and Wologdine's 1912 determination of the heat of formation of the calcium silicates and aluminates. |
| R. Nacken ... | 1922 | 1.428 | 40,323,000 | 10,000 | Direct determination by solution of materials in HCl and HF acids and measuring the thermal changes. |

By studying the Table it will be seen that the researches carried out between 1911 and 1922 enable us to form a fairly close estimate of the heat liberated in the exothermic reaction of clinkering, so that this problem, which during the last twenty years has been the subject of so much controversy, now appears to be well on the way to settlement. The correspondence of the last two values in the Table is remarkably close when we consider that they were obtained by entirely different methods using every resource of science in order to obtain exact results.

In addition to the exothermic reactions which occur (*a*) when the clay portion of the raw material has been dehydrated, but before sintering or clinkering takes place, and (*b*) when the decarbonated mixture combines to form cement clinker, there are in practice other reactions which give rise to the evolution of heat. Some of these it would be difficult or impossible to detect by means of a heat curve, as they would be masked by the possibly greater endothermic reactions proceeding at the same time.

The most important of them are mentioned below, but with the exception of the first they are not likely to be of great importance owing to the small percentages of the relative compounds. They do, however, all add their quota to the sum of the heat evolved.

(1) Combustion of any organic matter present naturally in the form of peaty matter, bitumen, or other carbonaceous matter. This may reach considerable proportions but may be regarded as the combustion of adventitious fuel.

(2) Oxidation of ferrous compounds to the ferric state. The heat evolved in the process of oxidising 1 gram of ferrous oxide (FeO) to ferric oxide (Fe_2O_3) is 455.4 gram calories, equivalent to 819.7 B.T.U.'s per lb., or 1,836,200 B.T.U.'s per ton, or 462,700 kilo calories per ton, or 0.06507 ton of coal (of 12,600 B.T.U.'s per lb.) per ton of ferrous oxide oxidised. From these data (the composition of the material being known) the value of the reaction per ton of clinker can be readily calculated.

(3) Oxidation of sulphides, usually ferrous sulphide (FeS), in clays containing organic matter, and pyrites (FeS_2) in rocks and in some clays and shales. The heat evolved in the oxidation of 1 gram of ferrous sulphide (FeS) to ferric oxide (Fe_2O_3) is 1,657 gram calories, equal to 2,982.5 B.T.U.'s per lb., or 6,681,000 B.T.U.'s per ton, or 1,684,000 kilo calories per ton, or 0.2367 ton of coal (of 12,600 B.T.U.'s per lb.) per ton of FeS oxidised. In the case of pyrites (FeS_2) the figures would be respectively 1,620 g. calories per gram, or 2,916 B.T.U.'s per lb., or 6,532,000 B.T.U.'s per ton, or 1,646,000 kilo calories per ton, or 0.2314 ton of coal (of 12,600 B.T.U.'s per lb.) per ton of FeS_2 completely oxidised to Fe_2O_3 and SO_2 .

The heat resulting from the combination of the liberated and oxidised sulphur with the lime present is 3,204.5 gram calories for each gram of sulphur, equivalent to 5,768 B.T.U.'s per lb., or 12,920,000 B.T.U.'s per ton, or 3,256,000 kilo calories per ton, or 0.4577 ton of coal (of 12,600 B.T.U.'s per lb.) per ton of sulphur originally combined with iron in the mixed raw material for cement.

(4) Combination of oxidised sulphur derived from the combustion of the fuel

used with the lime present. The heat evolved in the formation of 1 gram of calcium sulphate from lime, sulphur dioxide, and oxygen is 753.8 gram calories for each gram of calcium sulphate formed, equivalent to 1,357 B.T.U.'s per lb., or 3,040,000 B.T.U.'s per ton, or 766,000 kilo calories per ton, or 0.1077 ton of coal (12,600 B.T.U.'s per lb.) per ton of CaSO_4 formed.

From these data, taking the amount of calcium sulphate in the finished clinker and deducting therefrom the amount due to that originally present in the raw material and that derived from sulphides originally present in the raw material, the value of the reaction may be readily assessed.

It may sometimes happen when sulphides or calcium sulphate are present in the raw material, especially if in notable quantities, that there is less calcium sulphate in the finished clinker than these quantities would represent, in which case any heat evolution would be limited to the oxidation of the original sulphur and its combination with lime less the heat absorbed by decomposition of the deficient quantity of calcium sulphate.

The heat absorbed in decomposing 1 gram of calcium sulphate and liberating its lime is 753.8 gram calories, equivalent to 1,357 B.T.U.'s per lb., or 3,040,000 B.T.U.'s per ton, or 766,000 kilo calories per ton, or 0.1077 ton of coal (of 12,600 B.T.U.'s per lb.) per ton of CaSO_4 decomposed.

The heat evolved when 1 gram of ferrous carbonate (FeCO_3) is converted to ferric oxide and carbon dioxide is 73.8 gram calories, equivalent to 132.8 B.T.U.'s per lb., or 297,500 B.T.U.'s per ton, or 0.1054 ton of coal (of 12,600 B.T.U.'s per lb.) per ton of FeCO_3 decomposed.

Proposed Uruguayan State Factory.

THE project for the establishment of a State cement factory in Uruguay, which was approved by the National Administrative Council, has been vetoed by the President of the Republic. A two-thirds majority of votes in the Assembly of Deputies and Senators is now required for its sanction. The capital has been fixed at \$4,000,000 Uruguayan gold, equal to £800,000 sterling.

Owing mainly to the construction of new concrete roads on a large scale and to the employment of concrete in the building trades generally, there has been an enormous increase in the demand for Portland cement in Uruguay. Foreign manufacturers have difficulty in competing with the local product on account of the high import duties. The American owners of the one existing plant enjoy a virtual monopoly in the trade, and it is presumably with a view to adjusting this situation that the Government is proposing to build a State cement factory.

Uruguayan Tariffs.

A recent Uruguayan law establishes a tax of 2 centesimos per 50-kilo sack of cement sold by manufacturers or importers. This tax will be collected on imported cement at the time of clearing through customs until 600,000 pesos have been obtained.

Cement Trade in Egypt.

In a recent report on "The Economic and Financial Situation in Egypt,"* Mr. R. M. Turner (Commercial Secretary, Cairo) states that the consumption of cement in Egypt is developing fairly rapidly, the average annual consumption for the last two or three years being roughly 270,000 tons. Total imports of cement during the year under review amounted to 250,924 metric tons valued at £E.511,805, compared with 224,843 metric tons worth £E.472,174 in 1927. Of the chief supplying countries Yugo-Slavia remains in the first place with an import of 91,916 metric tons valued at £E.168,431, while Belgium, the next in order, contributed 76,544 metric tons valued at £E.146,367. The United Kingdom's share amounted to 41,596 metric tons worth £E.101,934, or almost double the import in 1927. Germany, on the other hand, who had previously occupied the third place, is now fourth and only just ahead of France, with an import of 13,898 metric tons valued at £E.29,526. In fact, Germany was the only supplying country of any importance in this business whose trade appreciably declined. Just over one-fourth of the cement consumed in Egypt is of local production while, apart from the supplying countries mentioned, small quantities were also imported from Italy, Poland, Russia and Denmark.

Up to the present local manufacture has been carried out by the Société Anonyme des Ciments d'Egypte at their works at Maassara, but a powerful Swiss group has just formed the Société Anonyme Ciment Portland Toura and is setting up a modern cement plant at Toura, near Maassara. The Toura factory may begin manufacture in about a year's time, but meanwhile the company is marketing its "Karnak" brand imported from Belgium. It is expected that when the Maassara plant has been improved and the Toura works are in operation the combined yearly output will be at least 180,000 tons. In addition to this a company, the principal interest in which is held by well-known Danish makers of cement-making machinery, are building a factory a little beyond Helouan, but it will be some time before these works can begin to function.

Maassara cement enjoys a good deal of support although it is neither used by the Egyptian State railways nor in large public works contracts, but it is given preference by most of the provincial authorities. It follows, therefore, that imports of cement will probably automatically decrease as the local output increases, quite apart from the probable influence which the proposed changes in the customs tariff will have upon the cement trade as a whole. While a progressive demand can still leave room for fairly large but relatively reduced imports, a high tariff wall may stimulate a further extension and possibly a certain grouping of local plants to the detriment of the import trade. The cost of manufacture in Egypt is helped by a schedule of railway transport rates framed particularly with the object of helping Egyptian-produced cement.

As no particular brand of cement is specified in public works the contractor is free to supply any quality that passes the test of the British Standard

* London : H.M. Stationery Office. Price 2s. 6d. net.

Specification for Portland Cement (1925 edition). The Suez Canal Company, who are large users of cement, will not suffer an exception to their own regulations, which only admit those brands that are on the list of the French Ministry of Public Works.

Belgian, German and Yugo-Slavian competitors have improved both their ordinary and their rapid-hardening grades, but none of them can match the respective British levels. Many private Egyptian builders are becoming familiar with British cement and show a preference for it.

The combined prices and freight rates quoted by Continental competitors are so low that they bring their average price to about 9s. per ton below United Kingdom quotations. Long credit is generally allowed by Continental suppliers, with the result that their agents can dispose of the cement on very easy terms. Cases have also occurred where Continental manufacturers have styled their brands under English names, but this practice does not deceive many buyers.

Company Report and Accounts.

Dunstable Portland Cement Co., Ltd.

The accounts of the Dunstable Portland Cement Company for the period from April 1, 1928, to June 30, 1929, show a net profit of £63,482, and a balance brought forward of £13,482. Out of the total of £76,964 there have been paid compensation to officials £9,100, and three half-yearly dividends to June 30 last on the preference shares, absorbing £40,500. The balance of £27,364 is carried forward, no dividend being proposed on the ordinary shares (against 5 per cent.). The company owns the whole of the issued share capital of Smeed, Dean & Co. (this comprises 250,000 ordinary shares of £1 each and 107,000 seven-and-a-half per cent. preference shares of £1 each, these shares being valued in the balance-sheet of the holding company at £575,750).

The net profit of Smeed, Dean & Co. for the period under review was £23,077. Dividends have been paid on the preference shares to November 30, 1928, amounting to £6,420, and on the ordinary shares for the year to June 30 last, amounting to £20,000,

while the carry forward is reduced from £19,051 to £8,833. These dividends have been included in the above-mentioned profit figure of the Dunstable Company.

The report states that there has been a substantial increase in the output and sales of both companies, but trading has continued to be adversely affected by competition. Towards the end of 1928 agreements were entered into with other cement manufacturers to improve sales conditions, but the benefit of these did not materially affect the trading for the period under review. In connection with the merging of the selling organization with that of the Red Triangle group, the assets of Young & Son have been sold to Wiggins-Sankey (Hammersmith), the chief selling medium of that group, at a capital loss to the company of £111,788, which has been written off out of reserves. It is stated that the Dunstable and Smeed, Dean companies benefit through the general sales organization of the group. The guarantee by Allied Cement Manufacturers of the Dunstable company's preference dividend has been extended by a further two years from January 1, 1929.

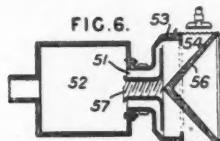
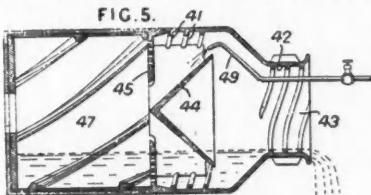
Swiss Capital Increase.

Portland Zementwerke Hausen A.G. is increasing its capital to five million francs (£198,000).

Recent Patent Applications.

Grinding, Crushing, etc., Mills.
KUENEMAX, J. R., 5522, Carlton Street, Oakland, California, U.S.A. August 21, 1929, No. 25511.

In a grinding mill comprising a horizontally disposed grinding chamber having a feed opening adjacent one end and delivery means at the opposite end, means are provided constantly to urge the material in the grinding chamber toward the feed end thereof, the finer particles of the material working out at the delivery end of the mill. The drum (6), Fig. 1, is lined with helical

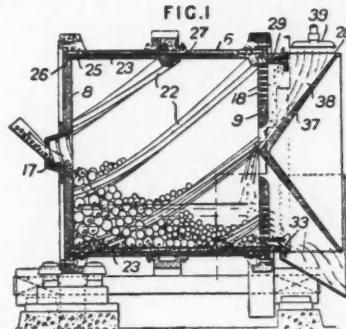


strips (23), one edge of each of which is provided with a recessed rib (22), the plain edge of the adjoining strip fitting into the recess together with a key (27), which wedges the strips together. The ends (25) of the strips engage in annular recessed portions (26) of the end plates (8, 9). The rotation of the drum (6) causes the ribs (22) to urge continuously the balls and large particles of unground material toward the end plate (8), which acts as a grinding surface for the material entering at (17). The end plate (9), through which the ground material is discharged, is provided with perforations (18) and oversize particles passing through the perforations are retained on a lipped ring (29) which is provided with outwardly flaring slots (33) through which the ground material passes to the screen (28). A conical member (37) is supported by radial ribs (38) from the ring (29) and the apex of the cone projects into a central perforation in the end plate (9) so that oversize particles from the screen (28) and

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ring (29) fall on the cone and are returned to the mill. A spray (39) may be used to clear the screen and cone during wet-grinding. When unsized material such as slimes is desired the ground material from the chamber (47), Fig. 5, passes through the perforations in the end plate (45) on to spiral ribs (41) which retain the heavier particles and drop them on the cone (44) for return to the mill. The pulp passes over further spiral ribs (42) in the discharge orifice (43) from which the heavier particles are wormed back to the ribs (41) for return to the mill. A water spray (49) may be used to clean the cone (44). The oversize return unit may be adapted to existing mills as shown in Fig. 6 in which an annular passage (51) is provided for the discharge from the grinding chamber (52) on to the lipped ring (53) and screen which are similar to those shown in Fig. 1. The oversize par-



ticles are raised by the vanes (54) and dropped on to the cone (56) for return to the grinding chamber through a passage (57).

Notes from the Foreign Press.

Abstracted by J. W. CHRISTELOW, B.Sc.

Hydraulic Index of Hydraulic Cements. H. LAFUMA. *Rev. Matériaux de Construction*, p. 241, July, 1929.

It is concluded that it is possible, in general, to define an index of hydraulic hardening and an index of chemical resistance based on the chemical composition of the cement. The hydraulic hardening index is $(\text{SiO}_2 + 0.2\text{Al}_2\text{O}_3)/\text{CaO}$, and the index of chemical resistance $(\text{SiO}_2 + \text{Al}_2\text{O}_3)/\text{CaO}$. The latter was wrongly proposed by Vicat as the hydraulic index.

The Silo Question in the Dry Process of Cement Manufacture. H. RICHARZ. *Tonind. Zeit.*, Vol. 53, p. 1,240, 1929.

To prevent the meal from caking at the bottom of the silo the author suggests a conical base of strong sheet metal which can be hammered to break up obstructions. The base of the silo should be fitted with a screw discharge capable of several speeds, and open to inspection. Silo lay-outs for various circumstances are described, including that reported on in CEMENT AND CEMENT MANUFACTURE for June, 1929, p. 179.

Effect of Zinc and Zinc Oxide on the Initial Hardening of Slag Cements.

PUJOL AND RENGADE. *Rev. Matériaux de Construction*, p. 289, August, 1929.

The addition of 0.01 per cent. ZnO has been found to lower appreciably the 2-day strength of slag cements, although the 7- and 28-day strengths were normal. The results obtained were irregular, e.g. the set may be retarded or accelerated with different samples of cement. It is, however, dangerous to mix slag or aluminous cements on a zinc-covered table.

Driving Cement Mills from Geared Motors. H. HERTEL. *Tonind. Zeit.*, Vol. 53, p. 1,245, 1929.

The driving of cement grinding mills by high-speed geared motors is on the increase. It is more economical than the use of low-speed motors or belt drives, and conserves space as compared with the latter. It is important to use only gears of the highest precision and best workmanship. The objection to geared motors held in some quarters is entirely due to the use of inferior gears. A number of modern high-speed geared motors are described. A recent advance is to combine motor and gear in one unit, the gear running in oil and on roller bearings.

Rotary and Vertical Driers. J. PRROUTEAU. *Rev. Matériaux de Construction*, p. 292, August, 1929.

An illustrated account of the rotary and vertical driers in use in the French cement and allied industries, more especially for drying coal.

A Simple Sedimentation Apparatus. KÜHL AND CZERNIN. *Tonind. Zeit.*, Vol. 53, p. 1,247, 1929.

The apparatus consists essentially of a 4-ft. vertical glass tube containing a column of alcohol. A cement-alcohol mixture is added by means of a special

apparatus at the top of the column, which is then sealed. The cement is graded by the larger particles sinking more rapidly than the smaller. To avoid convection a temperature fall is set up between top and bottom of the tube by means of electric heaters. A side tube near the bottom of the column connects through a capillary tube to a high reservoir of alcohol, the pressure from which slowly washes the suspension of cement in the lowest section of the column into a filter. The filters are changed at intervals and their contents estimated by ignition and weighing. One hour suffices to separate the cement into four fractions, the finest of diameter 25-15 μ . Reproducibility of results is not perfect in the case of the finest fraction, but the apparatus gives a satisfactory picture of the grading of a cement. It is to be placed on the market.

Feeding Raw Meal to the Rotary Kiln. E. SCHIRM. *Tonind. Zeit.*, Vol. 53, p. 1,263, 1929.

Descriptions are given of various methods of minimising the amount of raw meal carried away by the kiln exit gases in the dry process of cement manufacture. These methods may be divided into two main classes: (1) designing the upper end of the kiln so that the rate of evaporation of the moisture in the raw meal is reduced. This assists the formation of nodules of raw meal and prevents their disintegration; (2) briquetting the raw material with the addition of small quantities of water or tar as a binder. When the raw material is fed as meal, stoppage of the feeding tube may be avoided by using a screw feed to the tube, which is kept only partly filled and is sealed with meal at the lower end to prevent the escape of hot gases or introduction of cold air. Diagrams of the various designs are given.

Sieve Cloth and Sieve Analysis. H. HECHT. *Tonind. Zeit.*, Vol. 53, p. 1,265, 1929.

The importance of using sieve cloth which complies with the tolerances of the (German) standards is emphasised by the author's experiments. Such screens give reproducible results even when obtained from different sources. A number of cloths are sold, however, which purport to comply with the standards, but which in fact exceed the allowed tolerances. These give results which show serious differences from those given by truly standard cloth, and which do not agree among themselves.

Present-day Shaft-Kiln Practice. HAEGERMANN. *Tonind. Zeit.*, Vol. 53, p. 1,269, 1929.

During the past few years there has been a great increase in the capacity of the automatic shaft kiln due to the following improvements in practice: (1) The introduction of an air space between metal wall and refractory lining; the air for combustion is preheated (and the temperature of the clinkering zone reduced) by passing through this annular space; (2) the introduction of the air under pressure (up to 1,000 mm. water gauge) at the grate, and of subsidiary air at lower pressure at points above the grate; (3) use of recorders for air and exit gases; (4) introduction of the raw material mixed with fuel as small briquettes; (5) the use of a mixture of coke and anthracite, finely or coarsely ground.

Effect of the Fineness of Portland Cement on its Properties. P. FILOSOFOW.
Tonind. Zeit., Vol. 53, p. 1,302, 1929.

A Portland cement was separated into fine and coarse fractions (designated 1 and 7) by means of the 10,000 per sq. cm. sieve (=254 per linear inch). These fractions were mixed in the proportions (2) 9:1, (3) 7:3, (4) 5:5, (5) 3:7, (6) 1:9, and the mixtures tested for setting time and for strength, both neat and as 1:3 sand mortar. Setting time increased from 9½ hours for (1) to 19 hours for (7). Tensile strength, neat: Original cement, unsieved, 599 lbs. per sq. in. at 7 days, 940 lbs. at 28 days. The finest fraction (1) gives the greatest strength at 7 days (841 lbs.), but falls off considerably with age. At 28 days fraction (3) gives best results (966 lbs.) and retains its superiority with increasing age. In conclusion, if grinding is pushed too far, the tensile strength of the neat cement is lowered.

For 1:3 mortar, on the other hand, both tensile and compression results improve as the fineness of the cement is increased. Tensile strength: Original cement, 317 lbs. per sq. in. at 7 days, 412 lbs. at 28 days. Mixture (6), 114 lbs. at 7 days, 202 lbs. at 28 days. Mixture (1), 497 lbs. at 7 days, 513 lbs. at 28 days.

The residue on the 4,900 sieve (=180 per linear inch) was tested neat. It showed only slight tendency to harden in the early stages, but its strength increased considerably as time went on, and it ultimately attained a strength as great as that of fraction (1).

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